Intramolecular [4 + 2] Diels–Alder Cycloadditions of 2-Substituted Phosphabenzene and Arsabenzene in Triosmium Clusters

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Summary: 2-(Trimethylsilyl)-1-phosphabenzene and -1-arsabenzene, $Me_3SiC_5H_4E$ (E = P, As), react with $[Os_3H_2(CO)_{10}]$ to give the clusters $[Os_3H_2(Me_3SiC_5H_4E)(CO)_9]$, which contain σ-bonded, four-electron-donating μ_3-heterocyclic ligands, and the products $[Os_3H\{(Me_3Si)_2C_{10}H_9E_2\}(CO)_9]$, having tricyclic μ_3-ligands derived from [4 + 2] Diels–Alder cycloadditions.

Phosphabenzene and arsabenzene can coordinate through the heteroatom lone pairs as do pyridine and tertiary phosphines and arsines, through the π-system, or through both simultaneously.[1–3] We recently reported a new bonding mode for phosphabenzene as a σ-bonded, four-electron-donating μ_3-ligand in the cluster $[Os_3H_2(\mu_3\text{-}\eta^2\text{-}C_5H_5P)(CO)_9]$.[4] Pyridine behaves very differently in triosmium clusters and gives predominantly 2-pyridyl ligands by ortho metalation.[4,5]

We have now examined the corresponding reactions of 2-trimethylsilyl-substituted phosphabenzene and arsabenzene and have found a novel intramolecular [4 + 2] Diels–Alder cycloaddition process. Intramolecular [6 + 4] cycloaddition was observed in the reaction of 3,5-diphenylphosphinine or 1,3λ^3-azaphosphinines with diazomethanes[6,7] to yield diphosphachiropteradienes and diazadiphosphachiropteradienes, respectively. Also [(3,5-diphenylphosphinine)M(CO)$_5$] complexes (M = Cr, Mo, W) react with nitrilimines, nitrile oxides, and 1,3-dienes to give Diels–Alder cycloadducts.[8] Reactions of $[Os_3H_2(CO)_{10}]$ with 2-(trimethylsilyl)-1-phosphabenzene or -1-arsabenzene[9] (2 mol/mol of Os_3) in refluxing octane each give two major products, the clusters $[Os_3H_2(Me_3SiC_5H_4P)(CO)_9]$ (**1a**) and $[Os_3H\{(Me_3Si)_2C_{10}H_9P_2\}(CO)_9]$ (**2a**) from 2-(trimethylsilyl)-1-phosphabenzene and $[Os_3H_2(Me_3SiC_5H_4As)(CO)_9]$ (**1b**) and $[Os_3H\{(Me_3Si)_2C_{10}H_9As_2\}(CO)_9]$ (**2b**) from 2-(trimethylsilyl)-1-arsabenzene.[10] The organic ligands in **2a,b** are derived by intramolecular Diels–Alder cycloaddition of two heterocyclic ligands (Scheme 1).

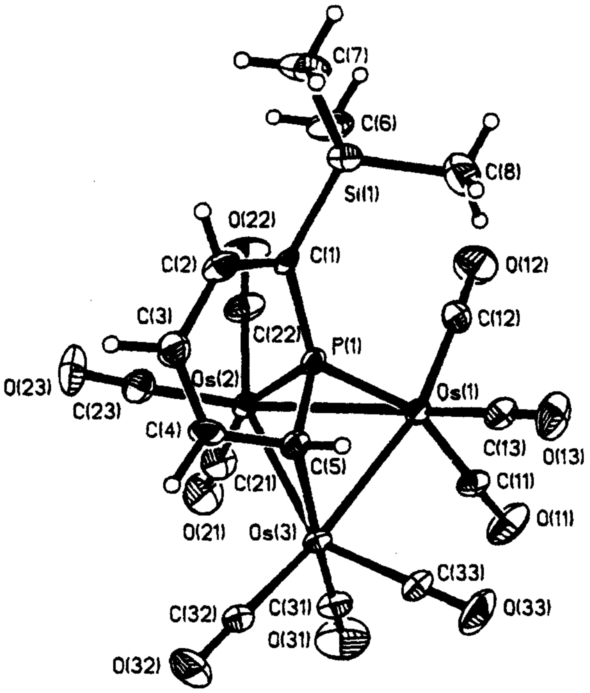

Figure 1. X-ray structure of the cluster $[Os_3H_2(Me_3SiC_5H_4P(CO)_9]$ (**1a**). Selected bond lengths (Å): Os(1)–Os(2), 2.893(2); Os(1)–Os(3), 2.823(2); Os(2)–Os(3), 2.944(2); Os(1)–P, 2.306(5); Os(2)–P, 2.347(4); Os(3)–P, 2.855(5); Os(3)–C(5), 2.19(2); P–C(1), 1.76(2); P–C(5), 1.76(2); C(1)–C(2), 1.318(4); C(2)–C(3), 1.45(3); C(3)–C(4), 1.32(4); C(4)–C(5), 1.47(3).

Clusters **1a,b** are isostructural with almost identical IR spectra around 2000 cm^{-1}. The X-ray structure of **1a** (Figure 1)[11] is quite unlike those of stoichiometrically related tertiary phosphines and tertiary arsines of the type $[Os_3H_2(CO)_9L]$ (L = tertiary phosphine or arsine) which are structurally related to $[Os_3H_2(CO)_{10}]$ as CO-substituted derivatives.[12] These clusters are purple, have L as a normal terminal two-electron donor, and are formally coordinatively unsaturated. In contrast, cluster **1a** has a four-electron μ_3-ligand and is coordinatively saturated. Bond distances and bond angles for

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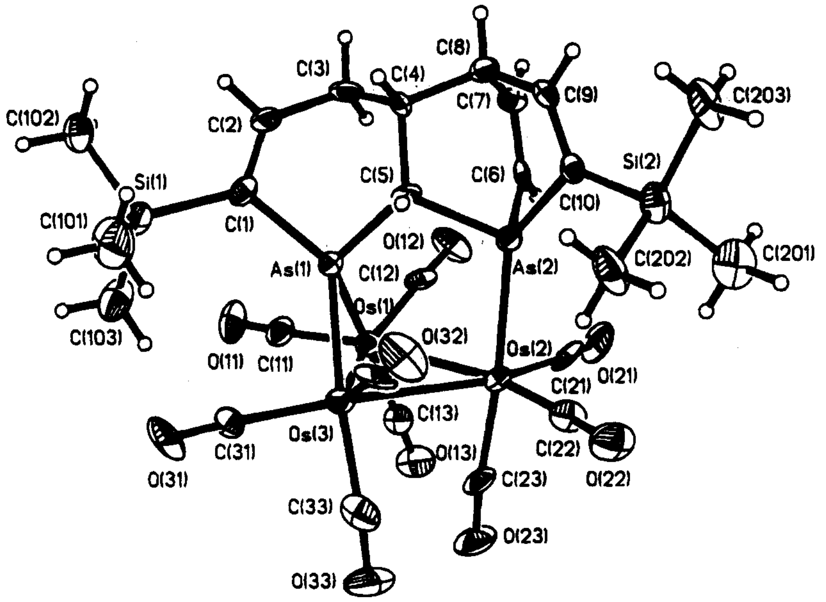
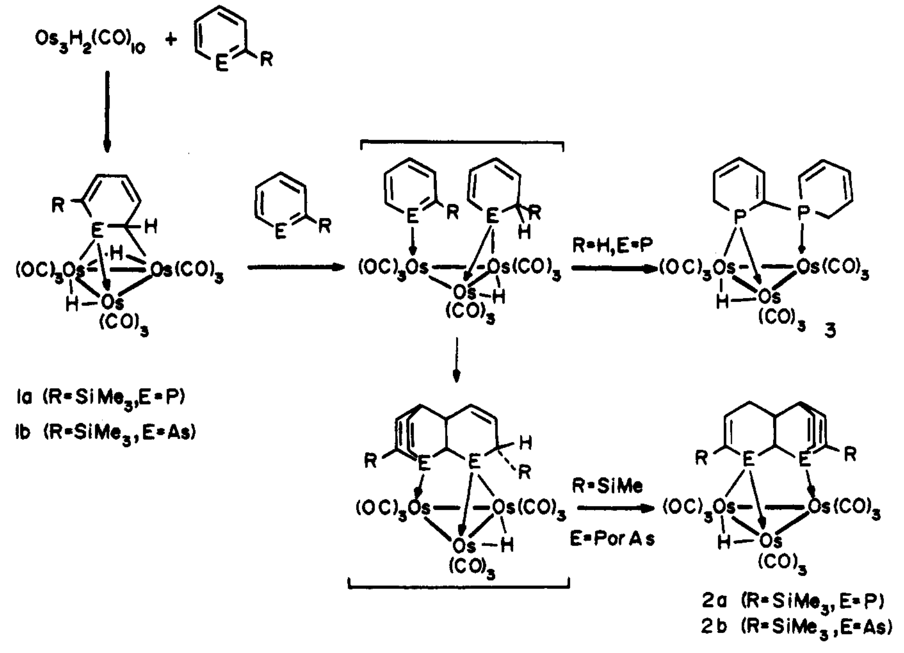


Figure 2. X-ray structure of the cluster $[Os_3H\{(Me_3Si)_2C_{10}H_9As_2\}(CO)_9]$ (**2b**). Selected bond lengths (Å): Os(1)—Os(2), 2.867(2); Os(1)—Os(3), 2.923(2); Os(2)—Os(3), 2.917(2); Os(1)—As(1), 2.470(2); Os(2)—As(2), 2.497(2); Os(3)—As(1), 2.469(2); As(1)—C(1), 1.96(2); As(1)—C(5), 1.94(2); C(1)—C(2), 1.30(3); C(2)—C(3), 1.53(3); C(3)—C(4), 1.50(3); C(4)—C(5), 1.55(2); C(4)—C(8), 1.55(3); As(2)—C(5), 1.95(2); As(2)—C(6), 1.87(2); As(2)—C(10), 1.98(2); C(6)—C(7), 1.36(3); C(7)—C(8), 1.47(3); C(8)—C(9), 1.49(3); C(9)—C(10), 1.32(3); Si—C(1), 1.86(2).

Scheme 1. Reactions of 2-(Trimethylsilyl)-1-phosphabenzene and 2-(Trimethylsilyl)-1-arsabenzene with $[Os_3H_2(CO)_{10}]$.



1a closely parallel those of $[Os_3H_2(2\text{-}^tBuC_5H_4P)(CO)_9]$ obtained similarly from 2-*tert*-butyl-1-phosphabenzene.[4] The hydride ligands (^1H NMR (CD_2Cl_2): δ −17.66, −19.25) were not located in the X-ray study but bridge the Os(1)—Os(2) and Os(2)—Os(3) edges on the basis of the metal−metal bond lengths and other ligand positions. At 220 K the hydride signals for **1a** are resolved into two sets (mole ratio 20:1). The minor isomer probably has hydrides along the Os(1)—Os(2) and Os(1)—Os(3) edges. The cluster **1b** is isostructural with **1a**, but the hydride ligands (^1H NMR ($CDCl_3$, 245 K): δ −17.49, −19.43) are not resolved into two sets of hydrides, indicating that either only one isomer is present or the corresponding fluxional process has not been frozen out.

For the cluster **2b** (X-ray structure, Figure 2),[13] the tricyclic ligand is coordinated through the arsenido bridging atom As(1) and through the tertiary arsine atom As(2) and, hence, behaves as a five-electron donor consistent with **2b** being a monohydride (^1H NMR (CD_2Cl_2): δ −18.70). The ring containing As(1) contains only one C=C bond, C(1)—C(2), and the ring containing As(2) has two C=C bonds: C(6)—C(7) and C(9)—C(10).

Clusters **2a,b** are also formed quantitatively by the reaction of **1a,b** with an excess of the appropriate ligand in refluxing *n*-octane. The mechanism of formation of the cycloadduct is unknown but requires various H atom shifts as well as formation of heteroatom (As or P)—C bonds and C—C bonds. Scheme 1 shows possible intermediates (shown in brackets) in the formation of the coupled products **2a**,**b** and the differently coupled product **3** obtained from phosphabenzene.[4]

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Supplementary Material Available: Text giving experimental details and spectroscopic data for all new compounds and tables of crystal data, data collection, and structure solution parameters, positional and thermal parameters, bond lengths, and bond angles for **1a** and **2b** (15 pages). Ordering information is given on any current masthead page.

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(10) **Reaction of [$Os_3H_2(CO)_{10}$] with 2-(trimethylsilyl)-1-phosphabenzene**: A solution of the ligand (59 mg, 0.26 mmol) and [$Os_3H_2(CO)_{10}$] (100 mg, 0.12 mmol) in cyclohexane (30 cm^3) was refluxed for 30 min. TLC workup (SiO_2; eluent pentane) gave yellow **1a** (60 mg, 51%) (crystals for X-ray structure from cyclohexane) and yellow **2a** (46 mg, 38%). **1a**: ν(CO) (C_6H_{12}) 2104 m, 2077 vs, 2049 vs, 2033 s, 2022 m, 2009 s, 1995 m, 1980 s cm^{-1}; ^{1}H NMR (CD_2Cl_2, 230 K) δ 6.81 (ddd, H^b), 6.70 (dd, H^d), 6.06 (m, H^c), 2.62 (br, dd, H^a), 0.12 (s, SiMe$_3$), −17.66 (d, H^e), −19.25 (dd, H^f) (at 220 K, two extra hydride signals were resolved at δ −17.83 and −18.63 for a minor isomer (mole ratio, major:minor 20:1)); ^{31}P{^{1}H} NMR (CD_2Cl_2, 296 K): δ −18.1 (s). Anal. Calcd (found) for $C_{17}H_{15}O_9Os_3PSi$: C, 20.56 (20.43); H, 1.52 (1.49). **2a**: ν(CO) (C_6H_{12}) 2079 m, 2050 vs, 2024 s, 1999 m, 1978 s, 1969 w, 1952 mw cm^{-1}; ^{1}H NMR (CD_2Cl_2, 296 K) δ 7.32 (dd, H^a), 7.10 (ddd, H^h), 6.98 (ddd, H^c), 6.82 (dddd, H^b), 4.03 (dddd, H^d), 3.28 (ddd, H^i), 2.82 (m, H^e), 2.37 (m, H^g), 1.97 (dddd, H^f), 0.22 (s, SiMe$_3$), 0.12 (s, SiMe$_3$), −18.42 (dd, H^j) (probable assignments); ^{31}P{^{1}H} NMR δ −11.5 (d, P^1), −88.4 (d, P^2). Anal. Calcd (found) for $C_{25}H_{28}O_9Os_3P_2Si_2$: C, 25.85 (26.08); H, 2.43 (2.55). **Reaction of [$Os_3H_2(CO)_{10}$] with 2-(trimethylsilyl)-1-arsabenzene**: A similar reaction gave yellow **1b** (47%) and orange-yellow **2b** (32%) (crystals for X-ray structure from dichloromethane−cyclohexane mixture). **1b**: ν(CO) (C_6H_{12}) 2102 m, 2076 vs, 2049 vs, 2030 s, 2021 s, 2007 vs, 1995 m, 1980 m cm^{-1}; ^{1}H NMR ($CDCl_3$, 245 K) δ 6.88 (dd, H^b), 6.54 (d, H^d), 5.92 (ddd, H^c), 2.74 (br, s, H^a), 0.10 (s, SiMe$_3$), −17.49 (s, H^e), −19.43 (d, H^f). Anal. Calcd (found) for $C_{17}H_{15}O_9Os_3AsSi$: C, 19.69 (19.55); H, 1.45 (1.41). **2b**: ν(CO) (C_6H_{12}) 2078 m, 2049 vs, 2023 s, 1997 m, 1979 s, 1965 w, 1951 mw cm^{-1}; ^{1}H NMR (CD_2Cl_2, 296 K) δ 7.04 (dd, H^h), 7.02 (d, H^a), 6.90 (ddd, H^b), 6.75 (dd, H^c), 4.15 (dddd, H^d), 2.95 (br, d, H^i), 2.77 (dddd, H^e), 2.34 (dddd, H^g), 1.85 (ddd, H^f), 0.18 (s, SiMe$_3$), 0.09 (s, SiMe$_3$), −18.70 (s, H^j) (probable assignments). Anal. Calcd (found) for $C_{25}H_{28}O_9Os_3As_2Si_2$: C, 24.03 (24.21); H, 2.25 (2.35).

(11) Crystal data and data collection and refinement details for **1a**: $C_{17}H_{15}O_9Os_3PSi$, $M_r = 992.908$, triclinic, $P\bar{1}$, $a = 9.136(3)$ Å, $b = 9.295(5)$ Å, $c = 15.040(5)$ Å, $\alpha = 104.34(3)^\circ$, $\beta = 105.05(3)^\circ$, $\gamma = 94.48(4)^\circ$, $V = 1181.1(8)$ Å^3, $Z = 2$, λ(Mo Kα) = 0.710 73 Å, direct methods (SHELXTL-PLUS), 5397 unique absorption-corrected data, $5 \le 2\theta \le 55^\circ$, $I_o \ge 3\sigma(I_o)$, 280 parameters (all non-H atoms anisotropic), $R = 0.069$, $R_w = 0.064$, Nicolet R3v/m diffractometer.

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(13) Crystal data and data collection and refinement details for **2b**: $C_{25}H_{28}As_2O_9Os_3Si_2$, $M_r = 1249.15$, monoclinic, $P2_1/n$, $a = 14.846(4)$ Å, $b = 11.307(5)$ Å, $c = 20.41(1)$ Å, $\beta = 100.50(3)^\circ$, $V = 3370(2)$ Å^3, $Z = 4$, λ(Mo Kα) = 0.710 73, direct methods (SHELXTL-PLUS), 5876 unique absorption-corrected data, $5 \le 2\theta \le 50^\circ$, $I_o \ge 3\sigma(I_o)$, 360 parameters (all non-H atoms anisotropic), $R = 0.065$, $R_w = 0.067$, Nicolet R3v/m diffractometer.